

# Progress in Photocatalysis of g-C<sub>3</sub>N<sub>4</sub> and its Modified Compounds

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**Abstract.** Recently, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a polymeric semiconductor has been widely used as a low-cost, stable, and metal-free visible-light-active photocatalyst in the sustainable utilization of solar energy, such as water splitting, organic photosynthesis, and environmental remediation, which has attracted world wide attention from energy and environmental relative fields. Base on analysis of structure and theoretical calculation, the reasons that g-C<sub>3</sub>N<sub>4</sub> can be used as a non-metallic catalyst were discussed in this paper. Some group's research jobs that metal-supported g-C<sub>3</sub>N<sub>4</sub>, metal-supported g-C<sub>3</sub>N<sub>4</sub>/organic semiconductor compound and heterogeneous junction adjust the semiconductor electronic band structure have been summarized. And the mechanism, effect factors, and research developments on the reaction of organic degradation by photocatalytic and splitting water for hydrogen revolution catalyzed by above-mentioned modified g-C<sub>3</sub>N<sub>4</sub> were emphatically analyzed. Finally, the prospects for the development of highly efficient g-C<sub>3</sub>N<sub>4</sub> based photocatalysts are also discussed.

## 1 Introduction

Along with the rapid development of modern industrialization in recent years, people's demand for energy is increasing day by day, consuming a large amount of non-renewable fossil fuels (such as coal, oil, and natural gas) and discharging greenhouse gases (such as CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub>) and toxic gases cause serious energy crisis and environmental degradation, which make human beings face severe survival challenges[1]. Solar energy is an inexhaustible one-time energy, which is one of the most interesting research topics. Finding suitable semiconductors as photocatalysts capable of converting solar energy is an important task in materials science. Most photocatalysts currently face the same problem[2]: (1) It can only respond to less than 5% of the solar radiation in ultraviolet light due to the wide band gap, and it has a low visible-light utilization of 47% of solar energy; (2) The potential of valence and conduction bands is difficult to meet the potential needs of various catalytic reactions at the same time; (3) Photogenerated electron-hole recombination is easy, quantum efficiency is very low. The light elements of group III and group V combine through 2p and 3p orbitals, which cause unique and diverse physicochemical properties due to their short atomic spacing. Carbon and nitrogen elements have only two atomic shells with small radius, which can form strong covalent bonds with each other, and can also form isotropic dense three-dimensional covalent mesh structure through quadruple coordination. Berzelius and Liebig synthesized a polymerized carbon nitride named it as a melon and carried out relevant reports for the first

time, which is the earliest known report on synthetic polymers. Since Liu and Cohen[3] put forward β-C<sub>3</sub>N<sub>4</sub> covalent crystal theoretically, carbon and nitrogen compounds have attracted the attention of scientists all over the world due to their excellent properties in optics and mechanics. Teter and Hemley[4] of Carnegie Institute, Washington, used conjugate gradient method to recalculate C<sub>3</sub>N<sub>4</sub>, and concluded that C<sub>3</sub>N<sub>4</sub> may have five structures (namely, alpha phase, beta phase, cubic phase, quasi-cubic phase, and graphite-like phase, respectively.). Among them, graphite-like phase of g-C<sub>3</sub>N<sub>4</sub> with non-toxic and visible light response (semiconductor band gap: 2.7 eV) and other properties is the most stable phase at room temperature, which makes it have a promising in the field of catalysis. The g-C<sub>3</sub>N<sub>4</sub> has attracted great attention in photocatalytic applications[5-8] (such as hydrogen production, organic synthesis and pollutant degradation) because of its outstanding advantages of high photocatalytic activity, good stability and low price of raw materials, especially metal-free materials. In this paper, the reaction principle, the main problems, research status and development trend of g-C<sub>3</sub>N<sub>4</sub> semiconductor photocatalysis are summarized.

## 2 Photocatalytic mechanism analysis of g-C<sub>3</sub>N<sub>4</sub>

g-C<sub>3</sub>N<sub>4</sub> is a typical polymer semiconductor, in which the C and N atoms are hybridized with sp<sup>2</sup> to form highly delocalized π conjugated system[9-11]. The g-C<sub>3</sub>N<sub>4</sub> is an electron-rich organic semiconductor, and the band gap between them is ~ 2.7 eV, which can absorb

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blue and purple light with wavelength less than 475 nm in the solar spectrum[9,12,13]. Among them, Npz orbitals form the highest occupied molecular orbital (HOMO) of g-C<sub>3</sub>N<sub>4</sub>, Cpz orbitals form the lowest unoccupied molecular orbital (LUMO) of g-C<sub>3</sub>N<sub>4</sub>. Analysis result shows that nitrogen atoms can be used as the preferred oxidation site for H<sub>2</sub>O decomposition to produce O<sub>2</sub>, while carbon atoms provide the reduction site for H<sup>+</sup> to H<sub>2</sub>. The electrons from the VB are excited to the CB, leaving holes in the VB when the light energy is greater than or equal to the gap of semiconductor photocatalyst. The electrons and holes produced by light can cause reduction and oxidation reactions, respectively. To satisfy the energy of water splitting, the bottom of the CB is negative to the reduction potential of water (0 V vs NHE at pH = 0), while the top of the VB must be positive to the oxidation potential of water (1.23 V vs NHE). Therefore, A minimum photoelectron energy required for a thermodynamic reaction must be up to 1.23 eV. The absolute values of the oxidation and reduction energy levels of H<sub>2</sub>O molecules calculated by the calculation method are located between the energy gap of g-C<sub>3</sub>N<sub>4</sub>[10]. In addition, compared with traditional TiO<sub>2</sub> photocatalyst, g-C<sub>3</sub>N<sub>4</sub> can also effectively activate molecular oxygen to produce superoxide radicals for photocatalytic conversion of organic functional groups and photocatalytic degradation of organic pollutants[14] or inhibit the formation of hydroxyl radicals with strong oxidation ability to avoid peroxidation of organic functional groups[15]. It can be used as visible photocatalyst for photocatalytic conversion of solar energy in theory.

### 3 Preparation, properties and photocatalytic study of metal-supported g-C<sub>3</sub>N<sub>4</sub>

g-C<sub>3</sub>N<sub>4</sub> with an energy gap of 2.7 eV, can be used as a non-metallic photocatalyst for hydrogen evolution and oxygen release under ultraviolet and visible light. The g-C<sub>3</sub>N<sub>4</sub> catalyst can show catalytic activity for reducing water hydrogen evolution reaction or oxygen release reaction without metal cocatalyst when suitable sacrificial electron acceptor or donor exists, respectively. However, the hydrogen evolution activity of pure g-C<sub>3</sub>N<sub>4</sub> fluctuates greatly, the yield of different reactors is different (0.1-4.0 μmol/h), which can be solved by modification with a small amount of metal (such as Pt etc.)[16]. The deposition of metals on the surface of g-C<sub>3</sub>N<sub>4</sub> can effectively capture photogenerated electrons in the CB, and can be used as the active sites of the reaction, thus increasing the catalytic yield. In addition, the structure of g-C<sub>3</sub>N<sub>4</sub> is filled with six unshared electron pairs of nitrogen atoms, making it an ideal place to house metal atoms. Therefore, metal loading is a feasible method to improve catalytic efficiency. Besides, metal loading can improve other properties of g-C<sub>3</sub>N<sub>4</sub> (such as permeability)[17].

Wang' research group [18] first used monocyanamide to prepare g-C<sub>3</sub>N<sub>4</sub> to decompose water under visible light (wavelength greater than 420 nm) to produce H<sub>2</sub>. The

rate at which unmodified g-C<sub>3</sub>N<sub>4</sub> releases H<sub>2</sub> varies from 0.1 mol/L to 4.0 mol/L, and the ability to release H<sub>2</sub> can be significantly changed by a small amount of doping Pt. The amount of H<sub>2</sub> released by Pt-g-C<sub>3</sub>N<sub>4</sub> with a mass fraction of 3.0% Pt is 10.7 mol/h, and 770 mol/h is released within 72 h. In the same year, Maeda et al. of the University of Tokyo[19] synthesized g-C<sub>3</sub>N<sub>4</sub> deposited by Pt, Pb, Rh, Ru and other noble metals by the method of photodeposition to conduct the experiment of reducing H<sub>2</sub>O to H<sub>2</sub>. 0.1 g of g-C<sub>3</sub>N<sub>4</sub> catalyst powder deposited with noble metal was put into 100 mL water, in which triethanol amine containing 10% volume fraction was used as sacrifice agent. Under visible light irradiation with a wavelength greater than 420 nm, Pt-g-C<sub>3</sub>N<sub>4</sub> with a mass fraction of Pt released H<sub>2</sub> at a rate of 7.3 mol/h, and Pd-g-C<sub>3</sub>N<sub>4</sub> with a mass fraction of Pd released H<sub>2</sub> at a rate of 5.3 mol/h. The yield of hydrogen evolution was increased by about 7 times when the surface of g-C<sub>3</sub>N<sub>4</sub> was loaded with Pt nanoparticles.

The results show that compared with the covalent bond fracture from the hydrogen-rich surface of g-C<sub>3</sub>N<sub>4</sub>, the hydrogen elimination from the surface of g-C<sub>3</sub>N<sub>4</sub> containing the Pt-H bond is easier. Di et al.[20] reported a principle that the Fermi level can be automatically adjusted to obtain negative voltage based on the special quantization charging properties of Au nanoparticles, and Au nanoparticles are deposited in the surface of g-C<sub>3</sub>N<sub>4</sub> semiconductor materials by deposition precipitation, optical deposition, injection and so on. The results show that Au/g-C<sub>3</sub>N<sub>4</sub> prepared by deposition precipitation method has high catalytic activity due to the formation of tight metal-semiconductor heterojunction. The surface of the g-C<sub>3</sub>N<sub>4</sub> loaded Au nanoparticles capture and store the electrons generated by the illumination matrix, which change the Fermi level and make it more negative. The process improves the transmission ability of electrons from the CB in the g-C<sub>3</sub>N<sub>4</sub> to the Au.

Researchers have found that cocatalytic coupling agents can be used as efficient photocatalysts in water splitting reactions. Pradhan et al.[21] synthesized g-C<sub>3</sub>N<sub>4</sub> hybridization (denoted as PtAu/g-C<sub>3</sub>N<sub>4</sub>) of bimetallic PtAu alloy nanoparticles by a simple solvent-thermal method. PtAu/g-C<sub>3</sub>N<sub>4</sub> hybrids have high light absorption ability, which leads to the formation of more carriers and better electron transport properties, thus making them have better photocatalytic activity. The contents of Pt and Au in bimetallic alloys were changed by changing the initial Pt and the concentration of Au precursors. Under the visible light irradiation with a wavelength of more than 420 nm, the H<sub>2</sub> generation rate is 1009 μmol/g/h, which is ten times of the hydrogen generation rate of g-C<sub>3</sub>N<sub>4</sub>, but also far more than Pt/g-C<sub>3</sub>N<sub>4</sub> (281 μmol/g/h) and Au/g-C<sub>3</sub>N<sub>4</sub> (253 μmol/g/h). The hydrogen production rate of PtAu/g-C<sub>3</sub>N<sub>4</sub> hybrid is 713 μmol/g/h after 5 h test, which still has high photocatalytic activity, thus achieving better stability.

## 4 Study on the sensitization of g-C<sub>3</sub>N<sub>4</sub> photocatalyst

g-C<sub>3</sub>N<sub>4</sub> photocatalyst can only absorb blue and purple light with energy greater than 2.7 eV in theory due to the  $\pi$  conjugated structural characteristics of the heptazine ring[12,13]. Therefore, how to expand the absorption wavelength of g-C<sub>3</sub>N<sub>4</sub> has become an important problem in photocatalytic research. So far, in addition to copolymerization modification and semiconductor doping, surface sensitization, such as dye sensitization and semiconductor sensitization, has also been developed to modify g-C<sub>3</sub>N<sub>4</sub> to improve its visible light utilization. However, the three highest occupied molecular orbitals (HOMOs) in g-C<sub>3</sub>N<sub>4</sub> itself have p symmetry characteristics, in which HOMO-3 is formed by the reverse combination of pz orbital of pyridine nitrogen. It conforms to the symmetry of the highest unoccupied p orbit in the Huxler benzene ring model. The electron structure can cause charge transfer, that is, charge transfer from g-C<sub>3</sub>N<sub>4</sub> to benzene ring, which causes "organic" activation of aromatic ring and provides necessary conditions for catalyzing a series of reactions of aromatic ring. If the lamellae of g-C<sub>3</sub>N<sub>4</sub> is infinitely large, and the activation will affect the defects with higher electron localization ability and the edge of the lamellae.

Zang' Group[22] prepared perylene tetracarboxylic diimides (PTCDIs)/Pt/g-C<sub>3</sub>N<sub>4</sub> photocatalyst that the loading of PTCDIs on the surface of Pt/g-C<sub>3</sub>N<sub>4</sub>. Compared with Pt/g-C<sub>3</sub>N<sub>4</sub>, PTCDIs/Pt/g-C<sub>3</sub>N<sub>4</sub> extends the range of visible light and produces hydrogen around ~0.375 mol/h in the presence of triethanolamine as a sacrifice agent, which is ten times higher than Pt/g-C<sub>3</sub>N<sub>4</sub> at  $\lambda > 420$  nm. Zeng' group[23] using fluorescein as photosensitizer has greatly improved the Ag/g-C<sub>3</sub>N<sub>4</sub> hydrogen production rate. And the synergies between the each composition best Ag load to endow them with excellent photocatalytic performance in the case of triethanolamine as sacrifice agent. Under the irradiation of sunlight to produce hydrogen rate of 2014.20  $\mu\text{mol/g}\cdot\text{h}$ , which is 4.8 times of not sensitized Ag/g-C<sub>3</sub>N<sub>4</sub>. Fan' group[24] used EY sensitization Au/g-C<sub>3</sub>N<sub>4</sub>, and confirmed that photogenerated electrons transferred from EY to the conduction band of g-C<sub>3</sub>N<sub>4</sub> would eventually be transferred to Au co-catalyst, thus inhibiting carrier recombination and effectively improving the photocatalytic hydrogen production activity. The hydrogen production rate is 660.8 mol/h·g under visible light  $\lambda > 400$  nm, which is 3.5 times of the hydrogen production rate of Au/g-C<sub>3</sub>N<sub>4</sub>. Wu' group[25] used fluorescein-sensitized Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite photocatalytic system, and the hydrogen production rate is 22.6 mol/h under visible light  $> 400$  nm, which is 19.3 and 3.8 times that of pure g-C<sub>3</sub>N<sub>4</sub> and unsensitized Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, respectively.

## 5 Application of g-C<sub>3</sub>N<sub>4</sub>-based heterojunction photocatalyst

In the modification method of g-C<sub>3</sub>N<sub>4</sub>, by constructing heterostructure with another type of semiconductor material, the advantages of multicomponent can be combined. The interface formed can reduce the recombination of photoinduced charge and improve the absorptivity of visible light. Meanwhile, the high redox ability of electrons and holes is maintained[26]. Therefore, design and synthesis of different types of g-C<sub>3</sub>N<sub>4</sub>-base heterojunction photocatalyst has important research value for achieving efficient photodegradation of pollutants and improving the increasingly serious environmental pollution[27]. In recent years, photocatalysts for type II-heterojunctions[28], g-C<sub>3</sub>N<sub>4</sub>-based p-n heterojunctions[29] and Z-scheme heterojunctions[30] have been developed rapidly and have shown great potential advantages in various photocatalytic systems. By constructing different types of heterostructures, the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> has been greatly improved.

At the interface between the two semiconductors, band bending will occur at the type II-heterojunction, forming a built-in electric field, and the photogenerated electrons and holes will migrate in reverse, thus reducing the recombination of photogenerated electrons and holes[31,32]. Li et al.[33] synthesized the hierarchical porous ZnO/g-C<sub>3</sub>N<sub>4</sub> composites with II-heterostructures by two-step method. The ZnO/g-C<sub>3</sub>N<sub>4</sub> can effectively degrade rhodamine B by improving the efficiency of charge separation. After exposure to UV lamp for 30 min, g-C<sub>3</sub>N<sub>4</sub> can photodegrade 93.8% of rhodamine, while ZnO/g-C<sub>3</sub>N<sub>4</sub> can degrade 100% of rhodamine B, showing excellent photocatalytic activity, and after five cycle tests, the degradation rate was still up to 95.2%. Moreover, X-ray diffraction spectrum showed that after cycling test, the structure of ZnO/g-C<sub>3</sub>N<sub>4</sub> has not changed, showing good durability. The separation efficiency of electron-hole pairs in p-n heterojunctions is faster than that of II-heterojunctions, and the photocatalytic activity is greatly improved compared with II-heterojunctions[34]. Cai et al.[35] prepared a new p-n heterojunction of g-C<sub>3</sub>N<sub>4</sub>/CuS photocatalyst by in situ synthesis technology. The degradation rate of g-C<sub>3</sub>N<sub>4</sub>/CuS heterogeneous for rhodamine B and methylene blue is 8.914 and 13.543 times for pure g-C<sub>3</sub>N<sub>4</sub>, and is 3.032 and 6.373 times for CuS, respectively. The enhancement of photocatalytic performance is attributed to the interaction between g-C<sub>3</sub>N<sub>4</sub> and CuS as well as the matching overlapping band structure. Under the irradiation of visible light, the charge carriers of CuS and g-C<sub>3</sub>N<sub>4</sub> can be excited simultaneously. The energy of the valence band of g-C<sub>3</sub>N<sub>4</sub> is lower than that of CuS, so the photogenerated holes in the valence band of CuS can easily migrate to the valence band of g-C<sub>3</sub>N<sub>4</sub>. Meanwhile, due to the conduction band energy of g-C<sub>3</sub>N<sub>4</sub> is greater than that of the CuS, the photogenerated electrons of g-C<sub>3</sub>N<sub>4</sub> on conduction band can be quickly transferred to the CuS conduction band, thus reducing the photogenerated

electrons and hole recombination. Liu et al.[36] constructed a new type of Z-scheme heterojunction photocatalyst (CDs/g-C<sub>3</sub>N<sub>4</sub>/MoO<sub>3</sub>) modified by carbon quantum dots. MoO<sub>3</sub>, as a typical p-type metal oxide semiconductor, is regarded as the best choice for constructing Z-scheme heterojunction photocatalyst due to its unique energy and electrochemical characteristics[37]. Carbon quantum dots (CDs) have excellent upconversion photoluminescence properties, as well as excellent photoluminescence transfer and reservoir properties, which contribute to the efficient use of visible light by catalysts[38]. After 90 min of visible light irradiation, MoO<sub>3</sub> and pure g-C<sub>3</sub>N<sub>4</sub> only degrade 10.1% and 5.3% of tetracycline, while CDs/g-C<sub>3</sub>N<sub>4</sub>/MoO<sub>3</sub> can degrade 88.4% of tetracycline. And after the three cycle operation, the degradation amount of tetracycline remained at 81.0%, and the structure of the catalyst did not change significantly after the photocatalytic reaction, which achieved excellent structural stability.

## 6 Summary and outlook

Addressing traditional photocatalyst of g-C<sub>3</sub>N<sub>4</sub> has the problems of small specific surface area, high exciton binding energy, serious photogenerated carrier recombination and large band gap, which can not make effective use of solar light. A large number of research work has been carried out on composition-structure-performance regulation of g-C<sub>3</sub>N<sub>4</sub>, and many important research results have been obtained, which has deepened an understanding of the nature and basic law of g-C<sub>3</sub>N<sub>4</sub> photocatalytic action. The next step study of photocatalysis laid a solid foundation[39].

In the future, the photocatalytic study of g-C<sub>3</sub>N<sub>4</sub> can be carried out from the following aspects. (1) g-C<sub>3</sub>N<sub>4</sub> photocatalyst was jointly modified by multiple methods. For example, combining copolymerization with nanostructure regulation can optimize the chemical composition of materials and regulate their semiconductor band structure, on the other hand, it can control the nanostructure and surface morphology of materials, so as to improve the kinetic process in multiple photocatalytic reactions. (2) The application of g-C<sub>3</sub>N<sub>4</sub> in photocatalysis was further expanded, especially in organic selective photosynthesis and CO<sub>2</sub> photocatalytic reduction. g-C<sub>3</sub>N<sub>4</sub> is suitable for selective conversion of organic functional groups and reduction fixation of CO<sub>2</sub> due to its unique band structure and material properties of organic semiconductors. (3) Theoretical calculations and experimental studies show that g-C<sub>3</sub>N<sub>4</sub> with suitable conduction and valence bands, which can be used as photocatalysts for fully hydrolyzed water. Hence, screening and designing suitable hydrogen and oxygen-producing cocatalysts for g-C<sub>3</sub>N<sub>4</sub> is expected to be realize photocatalytic total hydrolysis of water by surface modification and optimization of chemical reaction kinetics.

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